

Gelation Paradox

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Abstract

The gelation paradox first raised by Stockmayer is re-examined by comparing the extent of reaction in sol phase and that in the interior of gel. It is shown that the Stockmayer limit, $2/f$, for the extent of reaction is the lowest limit in gel phase, as well as being the highest limit for sol molecules.

Key Words: Extent of Reaction/ Interior of Gel/ Infinity

In this paper, we discuss the gelation paradox. The question was first raised by Stockmayer in 1949 [1], but formally has not been answered until today. The question associated with the paradox is, according to Stockmayer, as follows:

Consider the ideal branching process of the $R-A_f$ model. Assume the equal reactivity of functional units, but that no ring formation is allowed. Consider an x -mer molecule. This molecule has fx functional units and $2(x-1)$ reacted functional units, so that the extent of reaction of this molecule is $2(x-1)/fx$. Since gel is an infinitely large molecule, the extent of reaction in the interior of gel must be

$$p_{gel} = \lim_{x \rightarrow \infty} \frac{2(x-1)}{fx} \rightarrow \frac{2}{f} \quad (1)$$

It is apparent that the extent of reaction of the whole system can not exceeds $2/f$ because this is the upper limit for the gel phase to attain. Quite in contrast, according to the Flory formulation [2], the system easily exceeds this point and attains $p = 1$; hence one must conclude that the excess bonds beyond $2/f$ are due to ring formation. Quite aside from the fundamental logic involved in Flory's procedure, his formulation cannot be rigorous, for it predicts a very definite number of cyclic linkages in the system, although the initial assumptions do not specifically treat such structures in any way.

The above argument by Stockmayer reveals that the ideal branching theory that forbids ring formation in its initial assumption allows itself the occurrence of rings [4,5]; it shows that the classic theory includes the paradoxical logic that the conclusion contradicts the initial assumption. A purpose of this short paper is to give another explanation for the old question from a different point of view, since the question has revived repeatedly in the community, formally and informally.

Extent of Reaction in the Interior of Gel

Let us confine our discussion to the regime: $p_c \leq p \leq 1$. The extent of reaction of sol and gel can be defined by

$$p_{sol} = \frac{2 \sum_{x=1}^{\infty} (x-1)N_x}{f \sum_{x=1}^{\infty} xN_x} \quad (2)$$

$$p_{gel} = \frac{fM_0p - 2 \sum_{x=1}^{\infty} (x-1)N_x}{f \left(M_0 - \sum_{x=1}^{\infty} xN_x \right)} \quad (3)$$

It is known that the number distribution of x -clusters has the form:

$$N_x = M_0 \frac{f\{(f-1)x\}!}{x! \nu_x!} p^{x-1} (1-p)^{\nu_x} \quad (x = 1, 2, \dots) \quad (4)$$

where $\nu_x = (f-2)x + 2$ represents the number of unreacted functional units on an x -cluster. Let $\theta = p(1-p)^{f-2}$, then define the generating function:

$$A(\theta(p)) = \sum_{x=1}^{\infty} N_x / M_0 = \frac{(1-p)^2}{p} \sum_{x=1}^{\infty} \omega_x \theta^x \quad (5)$$

where $\omega_x = \frac{f\{(f-1)x\}!}{x! \nu_x!}$. The weight fraction of sol is, by definition,

$$W_{sol} = \sum_{x=1}^{\infty} xN_x / M_0 = \frac{(1-p)^2}{p} \sum_{x=1}^{\infty} x \omega_x \theta^x \quad (6)$$

Our aim is to calculate the quantity $A(\theta)$. For this purpose, define the other generating function:

$$\theta \frac{\partial M(\theta)}{\partial \theta} = \sum_{x=1}^{\infty} x \omega_x \theta^x \quad (7)$$

from which we have

$$M(\theta) = \sum_{x=1}^{\infty} \omega_x \theta^x + c_1 \quad (8)$$

In order to equate $M(\theta)$ with $\sum_{x=1}^{\infty} \omega_x \theta^x$, we put $c_1 = 0$. The boundary condition then becomes

$$M(\theta) |_{\theta=0} = M(\theta(p)) |_{p=1} = 0 \quad (9)$$

Solution for a Special Case of $f = 3$

Before proceeding with our discussion, let us consider the familiar problem [3]: Let Q be the probability that a chosen branch is finite. Then the following recurrence relation holds:

$$Q = 1 - p + pQ^{f-1} \quad (10)$$

which has the solutions: $Q = 1$ and

$$p(Q^{f-2} + Q^{f-3} + \dots + 1) = 1 \quad (11)$$

For $f = 3$, eq. (11) yields

$$Q = \frac{1-p}{p} \quad (12)$$

from which we have

$$W_{sol} = \sum_{x=1}^{\infty} xN_x / M_0 = \left(\frac{1-p}{p} \right)^3 \quad \text{for } p \geq p_c \quad (13)$$

Then using eqs. (6) and (7), we have

$$\theta \frac{\partial M(\theta)}{\partial \theta} = \frac{1-p}{p^2} \quad (14)$$

so that, by $\theta = p(1 - p)$ for $f = 3$, we have

$$\frac{\partial M(\theta)}{\partial \theta} = p^{-3} \quad (15)$$

Since $d\theta/dp = 1 - 2p$,

$$M(\theta(p)) = \sum_{x=1}^{\infty} \omega_x \theta^x = -\frac{1}{2p^2} + \frac{2}{p} + c_2 \quad (16)$$

Using the boundary condition, $M(p) |_{p=1} = 0$, we have $c_2 = -3/2$. Then substituting eq. (16) into eq. (5), we gain

$$A(\theta(p)) = \sum_{x=1}^{\infty} N_x/M_0 = \left(\frac{1-p}{p}\right)^3 \frac{3p-1}{2} \quad \text{for } p \geq p_c \quad (17)$$

By eqs. (2) and (3) along with eqs. (13) and (17), we can now express p_{sol} and p_{gel} as functions of p ; the result is

$$p_{sol} = 1 - p \quad \text{for } p \geq p_c \quad (18)$$

$$p_{gel} = \frac{p \left\{ 1 - \left(\frac{1-p}{p} \right)^4 \right\}}{\left\{ 1 - \left(\frac{1-p}{p} \right)^3 \right\}} \quad \text{for } p \geq p_c \quad (19)$$

The above solutions are plotted in Fig. 1. it is seen that while p_{sol} decreases linearly from $1/2$ at $p = p_c$ to 0 at $p = 1$, p_{gel} increases, starting from $p_{gel} = 2/3 = 2/f$ in question, monotonically to 1 at $p = 1$, quite in contrast to the equality given in eq. (1). Stockmayer argues that the excess bonds beyond p_c must be ascribed to ring formation within the gel phase.

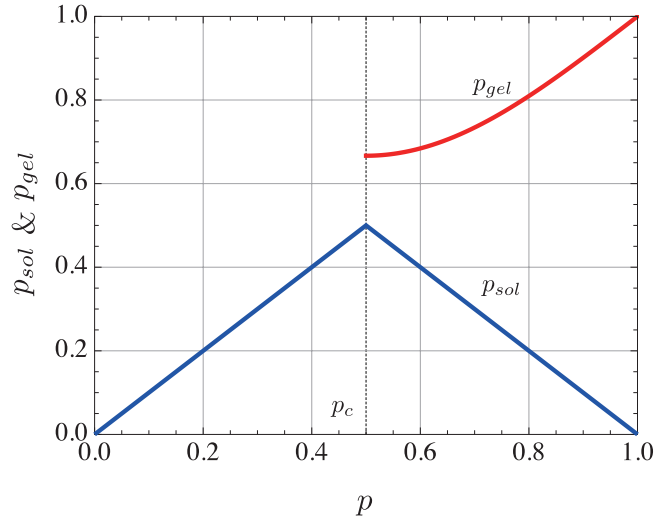


Fig. 1: The extent of reaction of sol and gel. p_{sol} is the theoretical line by eq. (18) and p_{gel} is that by eq. (19).

It is important to notice, however, that when we have the argument on eq. (1), we are talking about sol, because the equality $2(x-1)/fx$ itself assumes that the molecule has $(f-2)x+2$ unreacted functional

units, namely a finite molecule [6]. This reveals that the quantity $p = 2/f$ is the upper limit of p_{sol} , but not that of p_{gel} . It is the limiting point a largest sol molecule can attain.

The above argument becomes more apparent by making reference to Fig. 2. Since gel is an infinite molecule, it must possess, at least, one end that leads to infinity. This end must be counted as a reacted functional unit. In other words, the total number of the reacted functional units within gel must be larger than $2(x - 1) + 1$. Mathematically

$$p_{gel} \geq \lim_{x \rightarrow \infty} \frac{2(x - 1) + 1}{fx} = \frac{2}{f} \quad (20)$$

We realize that $p = 2/f$ is the lowest limit of p_{gel} , as well as being the highest limit for sol molecules. In mathematical terms it must be that

$$0 \leq p_{sol}^1 \leq 2/f \leq p_{gel} \leq 1 \quad (21)$$

where we use the notation p_{sol}^1 to express the extent of reaction for a single sol molecule and to distinguish from that, p_{sol} , for the whole sol phase. In contrast to the Stockmayer argument, the extent of reaction in the interior of gel must be greater than $2/f$, in accord with the result of Fig. 1. In the mathematical point of view, therefore, there is no paradox in the Flory formulation.

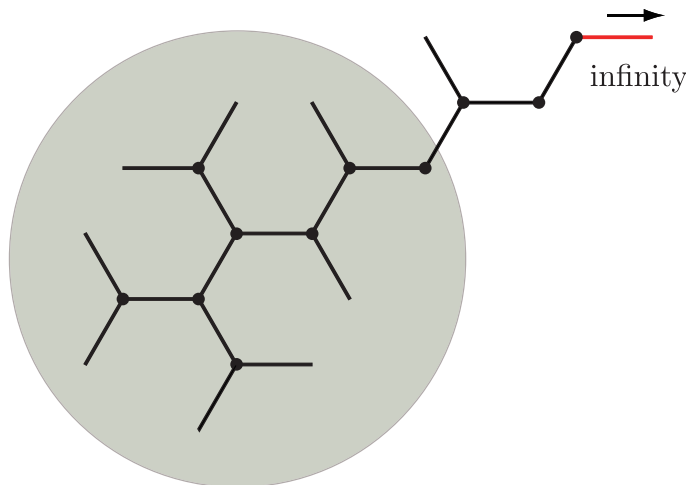


Fig. 2: An example of gel molecule. Note that at least one end must lead to *infinity*.

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